



# Enhancing catalytic activity of zeolitic octahedral metal oxides through zinc incorporation for ethane oxidative dehydrogenation

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## ABSTRACT

Zeolitic octahedral metal oxides possess both redox properties and microporosity, making them highly active for catalysis. Tuning the property of micropore by incorporating transition metal ion in the pore improves the catalytic activity greatly. In this study, single Zn species was incorporated into a micropore of a zeolitic octahedral metal oxide based on vanadomolybdate. Structural characterization demonstrated that the crystalline structure remained unchanged, and the micropores remained unblocked in the presence of Zn. Furthermore, this incorporation of Zn improved the catalytic activity of ethane oxidative dehydrogenation, achieving a 50 % of ethane conversion and 90% of selectivity. The yield of ethylene remained consistently at 45 % over 35 h, demonstrating the high stability of the catalyst. Mechanism study revealed that the isolated Zn site not only activated both O<sub>2</sub> and ethane, but also stabilized intermediates and transition states, leading to an increase in catalyst activity.

## 1. Introduction

Ethylene (C<sub>2</sub>H<sub>4</sub>) stands as a pivotal raw chemical compound with numerous applications in the manufacture of polymers, rubber, fiber, vinyl chloride, styrene, and other high-value products [1,2]. Ethane (C<sub>2</sub>H<sub>6</sub>) resides as one of the most prevalent constituents of natural gas and shale gas, exerting a strong greenhouse effect [3–5]. Direct emission of C<sub>2</sub>H<sub>6</sub> into the atmosphere precipitates air pollution and contributes to global warming. The conversion of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> turns this waste compound into a valuable chemical. The catalytic dehydrogenation of C<sub>2</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> offers several advantages over conventional C<sub>2</sub>H<sub>6</sub> steam cracking, including reduced energy consumption and lower greenhouse gas emissions [6–8]. There are two pathways for the catalytic dehydrogenation of C<sub>2</sub>H<sub>6</sub> into C<sub>2</sub>H<sub>4</sub>: non-oxidative dehydrogenation and oxidative dehydrogenation (ODH) [9,10]. Research has highlighted the advantages of C<sub>2</sub>H<sub>6</sub> ODH, such as its spontaneous process in thermodynamics, exothermic nature of reaction, and low temperature requirement.

Numerous catalysts have undergone development for C<sub>2</sub>H<sub>6</sub> ODH over the past few decades, mainly divided into two categories: molecular sieve supported catalysts and mixed metal oxides catalysts [5,11–13].

There are three types for mixed metal oxides catalysts: (i) noble metal containing catalysts [14,15]; (ii) non-reducible mixed oxides, including rare earth oxide-based catalysts [9,16–19], halide doped perovskites [20], alkali and alkaline-earth containing oxides [21]; (iii) reducible mixed metal oxides catalysts, including V and Mo-based mixed oxides [22], P and V-based oxides [23], Ni-based oxides [24–26], Cr-based oxides [19], and Co-based oxides [18,26–29]. However, it is essential to note that non-reducible mixed oxides, noble metal-containing catalysts, and molecular sieve supported catalysts do exhibit certain limitations such as high reaction temperature, high energy consumption, and low activity [13,30]. As a result, the ongoing research in ODH catalysts increasingly focuses on the development of catalysts with redox properties.

MoVTenb oxide is a particularly intriguing catalyst among those reported catalysts with redox properties for C<sub>2</sub>H<sub>6</sub> ODH [31–35]. Studies have demonstrated that this catalyst exhibits high C<sub>2</sub>H<sub>6</sub> conversion with good C<sub>2</sub>H<sub>4</sub> selectivity at 420 °C. The previous researcher has confirmed that the active site for C<sub>2</sub>H<sub>6</sub> ODH is located in the heptagonal channel. However, the heptagonal channel is obstructed due to partial occupation by transition metal ions, necessitating the relatively elevated reaction temperature [36,37].

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In contrast, Zeolitic vanadomolybdate (**VM**) catalyst successfully addresses this issue. The framework of **VM** is composed of pentagon units of  $(\text{Mo}_6\text{O}_{21})$  linked together by  $\text{MO}_6$  ( $\text{M} = \text{Mo}$  or  $\text{V}$ ), leading to a structural composition mainly composed of metal-oxygen octahedra - known as zeolitic octahedral metal oxides (ZOMOs) [38,39]. Notably, **VM** shares an isomorphic relationship with  $\text{MoVTenb}$  oxide, but in the case of **VM**, the pore blocking ions are removed, and the micropores are entirely open. This pivotal distinction leads to a high catalytic activity for **VM**, accompanied by a significantly reduced reaction temperature when compared to  $\text{MoVTenb}$  oxide [40]. Moreover, **VM** exhibits high structural and elemental diversity, with variations in properties and application performance attributed to its structure and chemical composition. By tuning the microenvironment of the heptagonal channel within **VM**, it becomes possible to achieve a substantial enhancement in catalytic activity [41].

In this work, we present the synthesis of a zinc vanadomolybdate-based ZOMO, denoted as **ZVM**, where the heptagonal channel of **VM** was tuned by incorporating isolated Zn ions. Structural analysis confirmed that Zn incorporation did not change the crystalline structure of the material; Zn occupied the wall of the heptagonal channel without blocking it. **ZVM** catalyzed the ODH of  $\text{C}_2\text{H}_6$  with high selectivity towards  $\text{C}_2\text{H}_4$  as the major product, even at low temperatures. Additionally, **ZVM** exhibited superior catalytic activity compared to **VM**. The stable nature of **ZVM** enabled long-term stability for  $\text{C}_2\text{H}_6$  ODH. The isolated Zn site activated  $\text{O}_2$  and  $\text{C}_2\text{H}_6$  while stabilizing intermediates and transition states, thereby contributing to the enhanced catalytic activity.

## 2. Experimental

### 2.1. Synthesis of Zn incorporated VM by a hydrothermal method

The synthesis of the catalyst was shown in Scheme S1.

#### 2.1.1. Synthesis of $(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$ (MAHM)

$(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$  (MAHM) was prepared by previously reported method [34]. First, 21.594 g of  $\text{MoO}_3$  (0.150 mol, 99.5 %, Aladdin) was dissolved in 33.2 mL of 25 %–30 % methylamine solution (methylamine: 0.210–0.251 mol, General-reagent). After  $\text{MoO}_3$  being completely dissolved, the solution was evaporated under vacuum ( $p/p_0 = 0.03$ ) at 75 °C, then a solid powder was obtained. The powder was dried in air at 80 °C overnight, and 26 g of MAHM was obtained.

#### 2.1.2. Synthesis of ZVM

First, MAHM (8.020 g, 4.42 mmol) were dissolved in 135 mL of water (Millipore grade) at 30 °C stirred for 10 min. Meanwhile  $\text{VOSO}_4$  (2.650 g, 99 %, 13.97 mmol) were dissolved in 45 mL of water (Millipore grade) at 30 °C and stirred for 10 min. Mixing the two aqueous solutions at 30 °C and stirred for 30 min.  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (0.805 g, 99 %, 2.8 mmol) were added to the mixture and stirred for 30 min. The pH of mixture was 2.8 and then removing the residual oxygen by  $\text{N}_2$  bubbling (100 mL/min) for 10 min. Then, the mixture was added into an autoclave with a 200 mL Teflon inner vessel with a thin Teflon sheet of 2000  $\text{cm}^2$ , and the autoclave was heated at 175 °C for 48 h in an oven. The crude solid (about 4.2 g) was isolated from the reaction mixture by filtration, washed with 1000 mL of water, and dried at 80 °C overnight.

#### 2.1.3. Purification of the catalyst

Adding 105 mL of an aqueous solution of oxalic acid (0.4 mol/L) into the crude solid, which was stirred at 60 °C for 30 min, followed by washing with 1000 mL of water (Millipore grade). The sample after the purification is abbreviated as **ZVM**, and the yield was 2.0 g. Elemental analysis for  $\text{Zn}_{1.1}[\text{Mo}_{30}\text{V}_{10}\text{O}_{112.8}] \cdot 9\text{H}_2\text{O}$ , calc: Zn 1.49; Mo, 53.13; V, 9.46. found: Zn, 1.32; Mo, 53.06; V, 9.39.

### 2.1.4. Catalysts with different V and Zn content

The catalysts with various Zn contents were prepared following the same procedure only with different  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  content in precursor solution. The catalysts are abbreviated as **ZVM-XZn** where X indicates molar ratio of Zn to V in precursor solution.

The catalysts with various V contents were prepared following the same procedure only with different  $\text{VOSO}_4 \cdot 7\text{H}_2\text{O}$  content in precursor solution. The catalysts are abbreviated as **ZVM-XV** where X indicates molar ratio of V to Mo in precursor solution.

### 2.1.5. Heat-treatment of the catalyst

**ZVM** was calcined in air,  $\text{N}_2$ , and  $\text{C}_2\text{H}_6$  for 2 h with a heating ramp of 10 °C/min, which was abbreviated as **ZVM-AX**, **ZVM-NX**, and **ZVM-EX**, where X = calcination temperature. Hydrogen calcination of **ZVM** was carried out under Hydrogen for 2 h which abbreviated as **ZVM-HX**, where X = calcination temperature. **ZVM** after calcinating sequentially air and  $\text{C}_2\text{H}_6$  for 2 h was abbreviated as **ZVM-AEX** (X = calcination temperature).

## 2.2. Synthesis of Zn incorporated VM by an impregnation method

Zn supported **VM** was synthesized by impregnation method.  $(\text{CH}_3\text{COO})_2\text{Zn}$  (0.183 g, 99 %, 1 mmol based on Zn) dissolved in distilled water (10 mL) was mixed with **VM** (2.360 g, 15 mmol based on Mo). The impregnation was performed and stirred for 6 h at room temperature. Then, the materials were dried at 80 °C overnight and calcined in air at 400 °C for 2 h. The material after calcination was abbreviated as **Zn-VM**; the yield was 2.5 g.

## 2.3. In situ IR measurements

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) measurements were performed with a Bruker Vertex 70 spectrometer equipped with a flow-cell. The samples were placed in the sample holder. Prior to the measurements, the samples were heated under  $\text{O}_2$  flow (10 mL/min) at 300 °C for 60 min. After the pre-treatment, the temperature of the samples was controlled, and  $\text{C}_2\text{H}_6$ ,  $\text{N}_2$ , or  $\text{O}_2$  were purged into the samples. The spectra were recorded.

## 2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractor with  $\text{Cu-K}\alpha$  ( $\lambda = 1.5418 \text{ \AA}$ ) radiation at room temperature (tube voltage: 40 kV, tube current: 40 mA). Fourier Transform Infrared Spectrometer (FTIR) was conducted on a Bruker Vertex 70 spectrometer. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha spectrometer. The binding energies were calibrated using the  $\text{C}_{1s}$  peak at 284.8 eV. Peak deconvolution for molybdenum oxidation ( $\text{Mo}^{6+}$ ), vanadium oxidation state ( $\text{V}^{4+}$  and  $\text{V}^{5+}$ ) and oxygen reduction state were conducted based on previous research [42]. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) analysis was carried out with an electron microscope (Sigma 300, Zeiss) equipped with an EDX detector (Oxford Xplore 50). Transmission electron microscope (TEM) with energy-dispersive X-ray spectroscopy (EDX) analysis was carried out with a JEOL JEM-F200 equipped with an EDX detector (JED-2300 T). Electron paramagnetic resonance (EPR) was carried out with a Bruker EMX PLUS. Differential scanning calorimetry (DSC) was carried out with NETZSCH DSC 200F3. The surface areas were measured by a Micromeritics 3flex sorption analyzer with  $\text{N}_2$  adsorption-desorption measurements at  $-196 \text{ }^\circ\text{C}$ . The samples were evacuated at 200 °C for 2 h before the measurements.

Temperature programmed oxidation (TPO) measurements were carried out on Belcat II. Before the measurements, the material was pre-treated at 300 °C for 1 h in  $\text{N}_2$  (25 mL/min) or in air (25 mL/min). The temperature was increased from 100 °C to 600 °C with a ramp of 10 °C/

min in O<sub>2</sub> flow (10 % of O<sub>2</sub> in He, 10 mL/min). The O<sub>2</sub> consumption during ramping step was measured by a thermal conductivity detector (TCD). C<sub>2</sub>H<sub>6</sub> adsorption and temperature programmed desorption (TPD) measurements were carried out on Belcat II. Before the measurements, the material was pre-treated at 100 °C for 1 h in He (25 mL/min). The desorption profile from 100 °C to 600 °C was recorded with TCD under He flow (20 mL/min). Temperature programmed C<sub>2</sub>H<sub>6</sub> reduction (TP-C<sub>2</sub>H<sub>6</sub>) tests were carried on ZVM and VM. Reaction conditions were as follow: catalyst weight; 0.5 g, reactant gas composition; C<sub>2</sub>H<sub>6</sub>/Ar = 1/20 (mol%), total flow rate; 21 mL/min, reaction temperature range from 100 °C to 500 °C at a rate of 10 °C/min. The products were analyzed by FID and TCD. Elemental compositions in the bulk were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Agilent 5110).

Rietveld refinement of ZVM was analyzed by the Rietveld diffraction program of GSAS. The initial structure was obtained from the previous reports [43]. All metal positions and pattern parameters were refined for obtaining the lowest  $R_{wp}$ . Atom positions are shown in Table S1.

## 2.5. Catalytic reaction

Catalytic tests for ODH of C<sub>2</sub>H<sub>6</sub> were carried out in a conventional vertical flow system with a fixed bed flow reactor. The catalysts (0.5 g, granularity: 20–30) were charged in the fixed bed flow reactor. Before the reaction, pre-heating step was carried out at 310 °C under a various flow (air, N<sub>2</sub>, and C<sub>2</sub>H<sub>6</sub>). Then, the reaction mixture of N<sub>2</sub>/O<sub>2</sub>/C<sub>2</sub>H<sub>6</sub> with molar ratio of 40/5/5 (total flow rate: 50 mL/min) was fed to the reactor. The reactor was heated at a rate of 10 °C/min ranging from 260 °C to 310 °C, and these conditions were kept for 60 min at every 10 °C with analysis of the reactants and products. The reactants and products were analyzed with an online gas chromatograph (GC) GC-2014 C equipped with both FID and TCD detectors. C<sub>2</sub>H<sub>6</sub> conversion, C<sub>2</sub>H<sub>4</sub> yield, selectivity and CO<sub>x</sub> selectivity were calculated based on the following equation:

$$\text{C}_2\text{H}_6 \text{ conversion (\%)} = \frac{\text{mole of C}_2\text{H}_6 \text{ reacted}}{\text{mole of C}_2\text{H}_6 \text{ fed}} \times 100\%$$

$$\text{C}_2\text{H}_4 \text{ yield (\%)} = \frac{\text{mole of C}_2\text{H}_4 \text{ produced}}{\text{mole of C}_2\text{H}_6 \text{ fed}} \times 100\%$$

$$\text{C}_2\text{H}_4 \text{ selectivity (\%)} = \frac{\text{mole of C}_2\text{H}_4 \text{ produced}}{\text{mole of C}_2\text{H}_6 \text{ reacted}} \times 100 \%$$

$$\text{CO}_x \text{ selectivity (\%)} = \frac{\text{mole of CO}_x \text{ produced}}{\text{mole of C}_2\text{H}_6 \text{ reacted}} \times \frac{1}{2} \times 100\%$$

To investigate the reaction mechanism of C<sub>2</sub>H<sub>6</sub> ODH, the stepwise reaction of C<sub>2</sub>H<sub>6</sub> ODH was carried out over ZVM and VM. The detailed steps were as follows: First, 0.5 g of catalysts were charged in the fixed bed flow reactor and the pre-heating step was carried out at 310 °C under Ar for 1 h. Then, catalysts were treated under a gas flow of 5 % of C<sub>2</sub>H<sub>6</sub>/Ar, 5 % of O<sub>2</sub>/Ar, and 5 % of C<sub>2</sub>H<sub>6</sub>/Ar at 310 °C in an alternating fashion, and the intensity of FID signal and TCD signal were recorded during the whole process. The carbon balance was over 97 % for each run.

## 2.6. Activation energy

Furthermore, in order to investigate the reason for difference of catalytic performance between ZVM and VM, the catalytic test was conducted at 250–265 °C, and the apparent activation energy was calculated by Arrhenius plots (Fig. S1). The catalytic rates can simplify to the following form of C<sub>2</sub>H<sub>6</sub> ODH rates:

$$r_{\text{ODH}} = k \times P_{\text{O}_2}^a \times P_{\text{C}_2\text{H}_6}^b$$

where a and b represent the reaction order of O<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> and k

represent the reaction rate constant, respectively. C<sub>2</sub>H<sub>6</sub> ODH rates as a function of O<sub>2</sub> pressure to the power of a and C<sub>2</sub>H<sub>6</sub> pressure to the power of b on catalysts are shown in Fig. S2. Regressing the obtained a and b to the form of C<sub>2</sub>H<sub>6</sub> ODH rates and thus get the reaction rate constant (k).

The apparent activation energy can be expressed in the form Arrhenius equation:

$$\ln k = \frac{-E_a}{RT} + \ln A$$

The lnk values derived from measured reaction rate constant (k) for C<sub>2</sub>H<sub>6</sub> on catalysts as a function of reciprocal temperatures are shown in Fig. S1. Regressing of obtained data to the form of Arrhenius equation and get apparent activation energy. The transport limitations and estimation errors are found to be negligible in the previous literature by using the method of Koros and Nowak [44,45] using the catalyst with the same crystalline structure of ZVM.

## 2.7. Modeling and simulation

Static binding energy and transition state energy were conducted on Density functional theory (DFT) calculations. Optimizing the structures of the materials was carried out with Vienna Ab initio Simulation Package (VASP) [46,47]. The PBE exchange-correlation functional based on generalized gradient approximation was employed [48]. The Plane wave basis sets used to approximate wave functions of valence electrons were included to a 400 eV kinetic energy cut-off. The projector-augmented wave (PAW) method was adopted to describe interactions between valence electrons and atom cores [49]. All calculations were spin-polarized. Gaussian smearing with a width of 0.1 eV was imposed for electron distributions near the Fermi Level. The electronic structures and geometries of structures were optimized until the energy differences between successive steps were less than  $1 \times 10^{-4}$  eV and  $1 \times 10^{-3}$  eV respectively. For modeling the dispersion interactions, the DFT-D3 method was adopted [50]. The number of layers is two because the van der Waals interaction between C<sub>2</sub>H<sub>6</sub> in two neighboring layers was negligible (Fig. S3). The  $1 \times 1 \times 2$  unit cell used for simulation. The  $1 \times 1$  unit cell with a corresponding  $1 \times 1 \times 2$  Gamma k-point mesh generated by post-processing VASPKIT package was used [51,52]. The reaction of C<sub>2</sub>H<sub>6</sub> ODH was simulated in the heptagonal channel, which was in good agreement with the previous literature [53,54]. The charge densities difference was calculated using the VASPKIT package. Complete linear synchronous transit (LST) method was adopted to generate an initial pathway from the reactant to the product in the unit cell [55]. The barrier energies were obtained using the climbing image nudged elastic band (cINEB) method [56,57]. Activation energy calculation predicted the energy difference between the transition state and the energy of the system with molecule in the cavity.

$$\Delta E_t = E_{ts} - E_{(\text{material} + \text{molecule})}$$

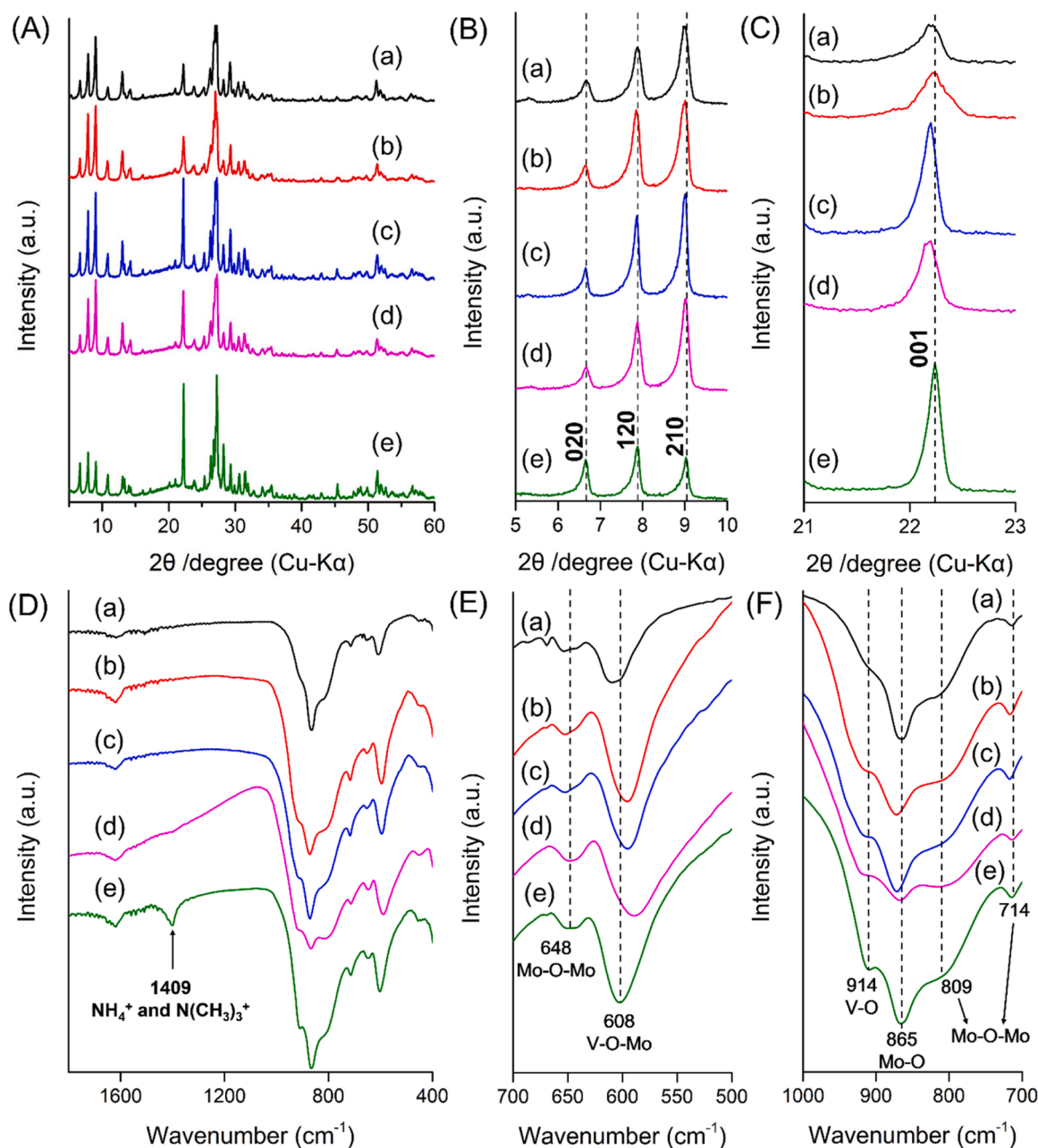
where  $\Delta E_t$  is the activation energy based on DFT calculation,  $E_{ts}$  is the energy of transition state, and  $E_{(\text{material} + \text{molecule})}$  is the energy of the material with adsorbed molecule.

## 3. Results and discussion

### 3.1. Materials synthesis and characterization

ZVM was synthesized using a hydrothermal method. A soluble Mo source of MAHM was prepared by dissolving MoO<sub>3</sub> in an aqueous solution of methylamine. VOSO<sub>4</sub> was used as the V source and added to the MAHM solution. ZnSO<sub>4</sub>·7 H<sub>2</sub>O was also added to the mixture. After the hydrothermal synthesis, the resulting raw solid was purified using a 0.4 mol/L aqueous solution of oxalic acid at 60 °C. This process yielded well-crystallized ZVM.

The XRD patterns of ZVM and VM are shown in Fig. 1 A. The XRD pattern of ZVM exhibited characteristic peaks at (020), (120), (210),



**Fig. 1.** (A) XRD patterns, (B) enlarged patterns in 5–10 degree, (C) enlarged patterns in 21–23 degree, (D) FTIR spectra, (E) enlarged FTIR spectra in 700–500  $\text{cm}^{-1}$ , and (F) enlarged FTIR spectra in 1000–700  $\text{cm}^{-1}$  of (a) ZVM, (b) ZVM-N300, (c) ZVM-A300, (d) ZVM-E300, and (e) VM.

(001), and other positions that were consistent with those of the crystalline orthorhombic VM (Fig. 1B) [41]. These results confirmed that the crystalline structure of ZVM and VM was the same. There was a new diffraction peak at 5.3 degree attributed to the (110) plane, which might be caused by Zn incorporation. The observed peak shift to a lower angle of ZVM suggested that the lattice parameter of ZVM was slightly larger than that of VM (Fig. 1B,C), which indicated that incorporating Zn into the VM framework caused expansion of the lattice parameter (Table S2).

The FTIR spectra of ZVM and VM showed that the peaks at 914  $\text{cm}^{-1}$  attributing to V-O, 865  $\text{cm}^{-1}$  attributing to Mo-O, 809, 714, and 648  $\text{cm}^{-1}$  attributing to Mo-O-Mo, and 608  $\text{cm}^{-1}$  attributing to V-O-Mo, respectively (Fig. 1 C) [40]. The IR bands below 1000  $\text{cm}^{-1}$  of ZVM and VM were similar, suggesting a similar bonding state between the materials. However, a shift in the IR band at ca. 608  $\text{cm}^{-1}$  was observed in ZVM, indicating a change in the bonding state due to Zn incorporation

(Fig. 1D). The IR band at about 1400–1409  $\text{cm}^{-1}$ , attributed to  $\text{NH}_4^+$  and  $\text{N}(\text{CH}_3)_3^+$ , originating from the metal precursor salts, was not observed in ZVM, which indicated that there was almost no  $\text{NH}_4^+$  and  $\text{N}(\text{CH}_3)_3^+$  in ZVM. Zn probably replaced  $\text{NH}_4^+$  and  $\text{N}(\text{CH}_3)_3^+$ .

ZVM and VM were characterized by SEM, showing that both materials exhibited a rod shape with the size of ca. 100 nm in a diameter and varying lengths (Fig. 2A,B). Zn incorporation in VM did not change the morphology of the material. Elemental distribution of the material was characterized by SEM-EDX mapping. The result showed that Mo, V, and Zn were uniformly distributed within the crystal particle (Fig. 2C,D,F), indicating that Zn was incorporated intrinsically into the structure. Elemental composition of the material was calculated based on ICP-AES. The result showed that Mo: V: Zn = 1: 0.322: 0.036.

XPS analysis was conducted to confirm the oxidation state of the metal elements in ZVM (Fig. 3). The XPS spectra of Mo showed peaks at



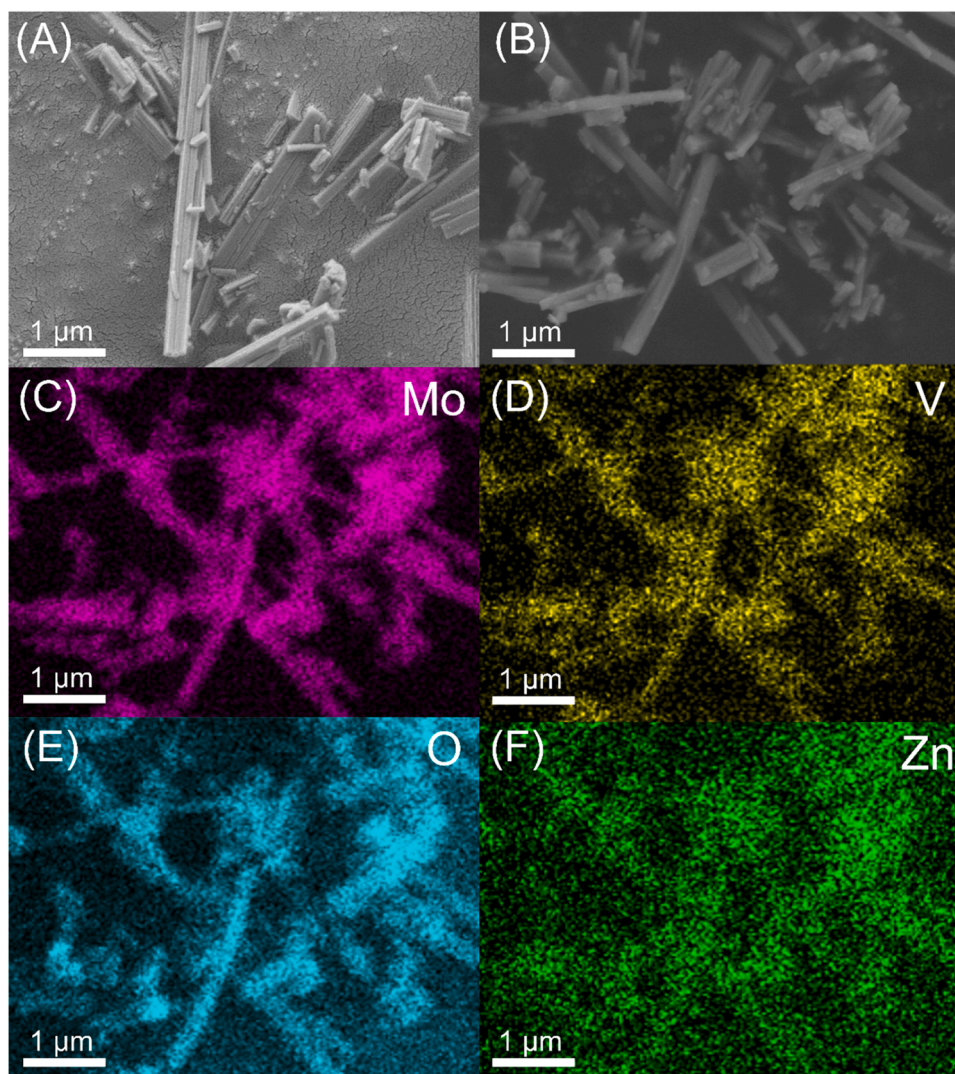


Fig. 2. SEM image of (A) VM, SEM image of (B) ZVM and corresponding elemental mapping images of (C) Mo, (D) V, (E) O, and (F) Zn.

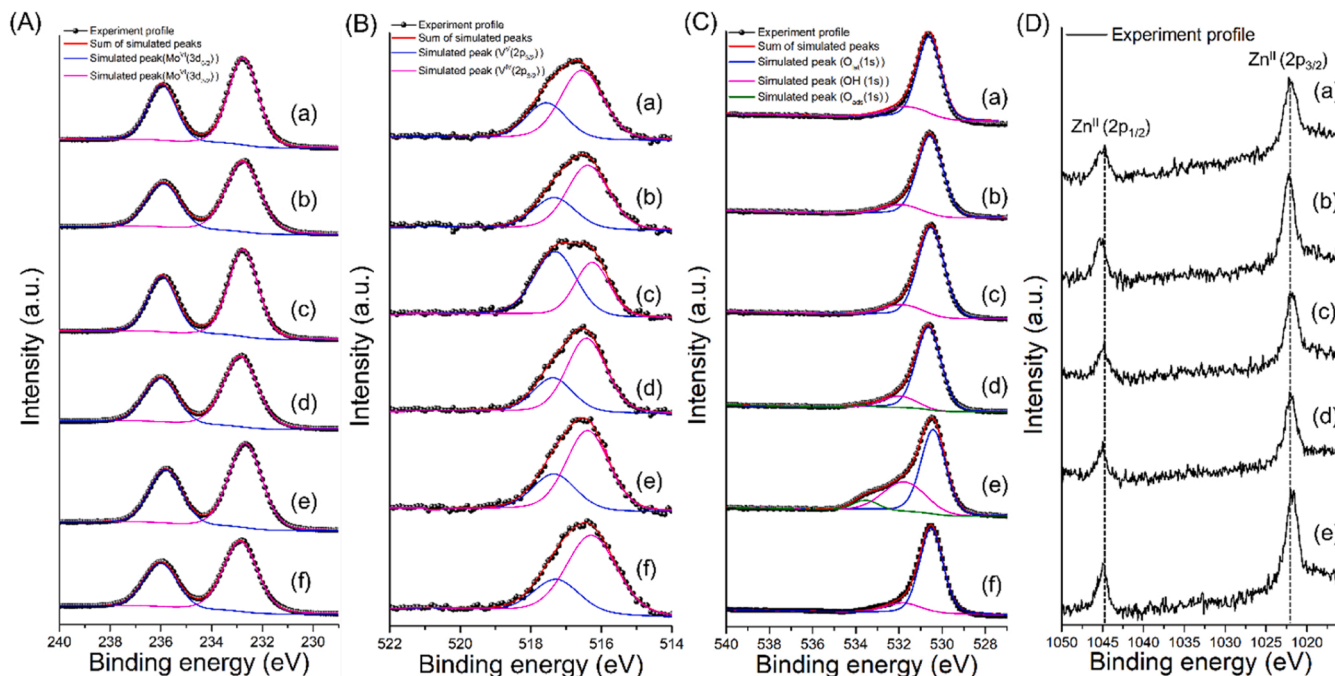
ca. 232.9 eV and ca. 236.0 eV, corresponding to Mo ( $3d_{5/2}$ ) and Mo ( $3d_{3/2}$ ), respectively (Fig. 3Aa). These peaks indicated that the Mo species was primarily in the + 6 oxidation state [58]. The corresponding V profile was fitted by two simulated peaks at ca. 516.4 eV and ca. 517.4 eV (Fig. 3B), attributing to  $V^{4+}$  and  $V^{5+}$  [59]. The ratio of  $V^{5+}/V^{4+}$  in ZVM was 0.50, which was higher than that in VM (0.38) (Fig. 3Ba,f). Zn was  $Zn^{2+}$  in ZVM. Based on the elemental analysis and oxidation states analysis, the chemical formula of the material was proposed to be  $Zn_{1.1}^{2+}[Mo_{30}^{6+}V_{6.6}^{4+}V_{3.4}^{5+}O_{112.8}]\cdot 9H_2O$ .

The position of Zn in ZVM was determined by the Rietveld refinement combined with DFT calculation. The good agreement between the simulated XRD pattern and the experimental pattern obtained from Rietveld refinement demonstrated that the proposed structures were correct (Fig. 4). Atomic position of ZVM after Rietveld refinement was shown in Table S1. There were majorly two positions in the material for locating Zn, the heptagonal channel (site 1, 2, 3, 4, 5, 6, and 7) and the hexagonal channel (site 8, 9, 10, 11, 12, and 13) (Fig. 4A). The refinement indicated that Zn was in the heptagonal channel of the material. The energies of the material with Zn in different positions in the heptagonal channel and hexagonal channel were evaluated by the DFT calculation (Fig. 4C). When Zn located in site 1, the system energy was the lowest, indicating that the site was the most possible site for Zn location (Fig. 4C). Zn located in the heptagonal channel and embedded in the wall of the micropore.

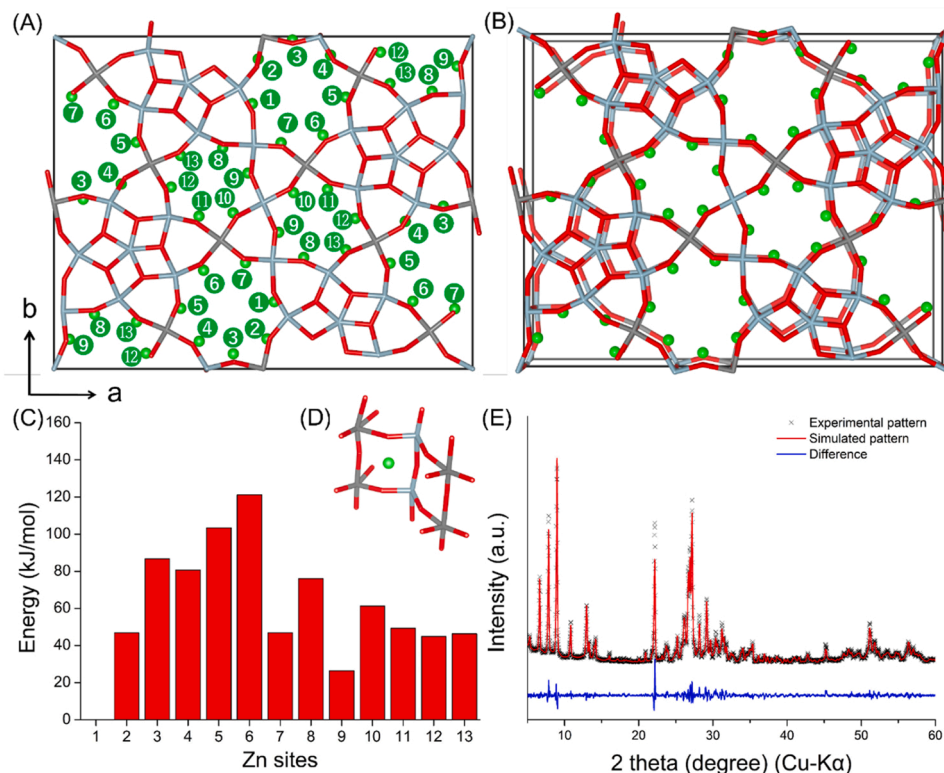
The thermal stability of ZVM was evaluated by heating it under various conditions. ZVM was found to be stable in both air and  $N_2$  at 400 °C, as evidenced by the unchanged XRD patterns and FTIR spectra after treatment (Fig. S4). While heating ZVM in  $H_2$  at 400 °C resulted in damage to its crystalline phase, reducing the treatment temperature to 300 °C preserved the crystalline phase.

The microporosity of ZVM was studied by the  $N_2$  adsorption-desorption and  $CO_2$  adsorption-desorption measurements (Fig. S5). The BET surface area, external surface area, and the micropore volume (Table S2) were calculated based on the adsorption isotherms of  $CO_2$ . The adsorbed volume of  $CO_2$  of ZVM was similar to that of VM, confirming that the presence of Zn would not block the micropore of the material. Increasing the Zn content in the synthesis did not change the adsorption volume of  $CO_2$ , and the micropore was not blocked (Fig. S5).

Furthermore, the Zn content was able to be varied by controlling the Zn content of the precursor solution. The results showed that the orthorhombic phase formed for Zn content (molar ratio of Zn to V in the precursor solution) of 0.15, 0.20, 0.25, and 0.30 (Fig. S6). Further increasing the Zn content or decreasing the Zn content would cause the generation of amorphous phase, such as the catalysts with the Zn content of 0.10 and 0.40 (Fig. S6Aa,f). Additionally, the V content was modulated by adjusting the V concentration in the precursor solution. The orthorhombic phase was synthesized with V content (molar ratio of V to Mo in the precursor solution) of 0.35, 0.40, 0.45, 0.50, 0.55, and



**Fig. 3.** XPS of (A) Mo of (a) ZVM, (b) ZVM-N300, (c) ZVM-A300, (d) ZVM-E300, (e) ZVM-AE300, and (f) VM, (B) V of (a) ZVM,  $V^{5+}/V^{4+}=0.50$ , (b) ZVM-N300,  $V^{5+}/V^{4+}=0.48$ , (c) ZVM-A300,  $V^{5+}/V^{4+}=1.44$ , (d) ZVM-E300,  $V^{5+}/V^{4+}=0.46$ , (e) ZVM-AE300,  $V^{5+}/V^{4+}=0.45$ , and (f) VM,  $V^{5+}/V^{4+}=0.38$ , (C) O of (a) ZVM,  $O_{lat}/OH = 1/0.140$ , (b) ZVM-N300,  $O_{lat}/OH = 1/0.150$ , (c) ZVM-A300,  $O_{lat}/OH = 1/0.146$ , (d) ZVM-E300,  $O_{lat}/OH/O_{ads} = 1/0.167/0.015$ , (e) ZVM-AE300,  $O_{lat}/OH/O_{ads} = 1/0.556/0.104$ , and (f) VM,  $O_{lat}/OH = 1/0.145$ , (D) Zn of (a) ZVM, (b) ZVM-N300, (c) ZVM-A300, (d) ZVM-E300, (e) ZVM-AE300.



**Fig. 4.** Structure models of (A) and (B) VM framework with different sites for locating Zn, (C) relative energy of Zn in different sites, (D) enlarged model of Zn location, and (E) Comparison of the simulated XRD based on the Rietveld refinement with the experimental XRD with  $R_{wp} = 11.05\%$ , Mo (blue), V (gray), O (red), Zn (green).

0.60 (Fig. S7). Excessive or low V content prevented the formation of crystals, such as the catalysts with V content of 0.35 and 0.60 (Fig. S7Aa, f).

### 3.2. $C_2H_6$ oxidation to $C_2H_4$

$C_2H_6$  ODH was carried out over the **ZVM** catalyst at each reaction temperature under atmospheric pressure. The activity of the reaction increased with the reaction temperature (Fig. 5A,B). The conversion of  $C_2H_6$  over the catalyst was low (16 %) at a low reaction temperature (260 °C), and the selectivity to  $C_2H_4$  was over 95 %. The conversion increased with the increase in reaction temperature.  $C_2H_6$  conversion of 49 % was achieved with  $C_2H_4$  selectivity of 92 % at 300 °C, finally. Compared with **VM**, **ZVM** exhibited higher activity over the entire selected temperature range, although both of them possessing the orthorhombic structure. The result demonstrated that Zn significantly enhanced the catalytic activity of the catalyst.

Zn was found to be critical for achieving high activity in the reaction. The  $C_2H_6$  ODH was catalyzed by **ZVM** with varying Zn contents at 310 °C (Fig. S8). Increasing the Zn content of the catalyst within a certain range increased the  $C_2H_6$  conversion, while excessive or low Zn content decreased reaction activity with keeping almost the same selectivity to  $C_2H_4$  (Fig. S8). The results highlight the importance of Zn in the reaction.

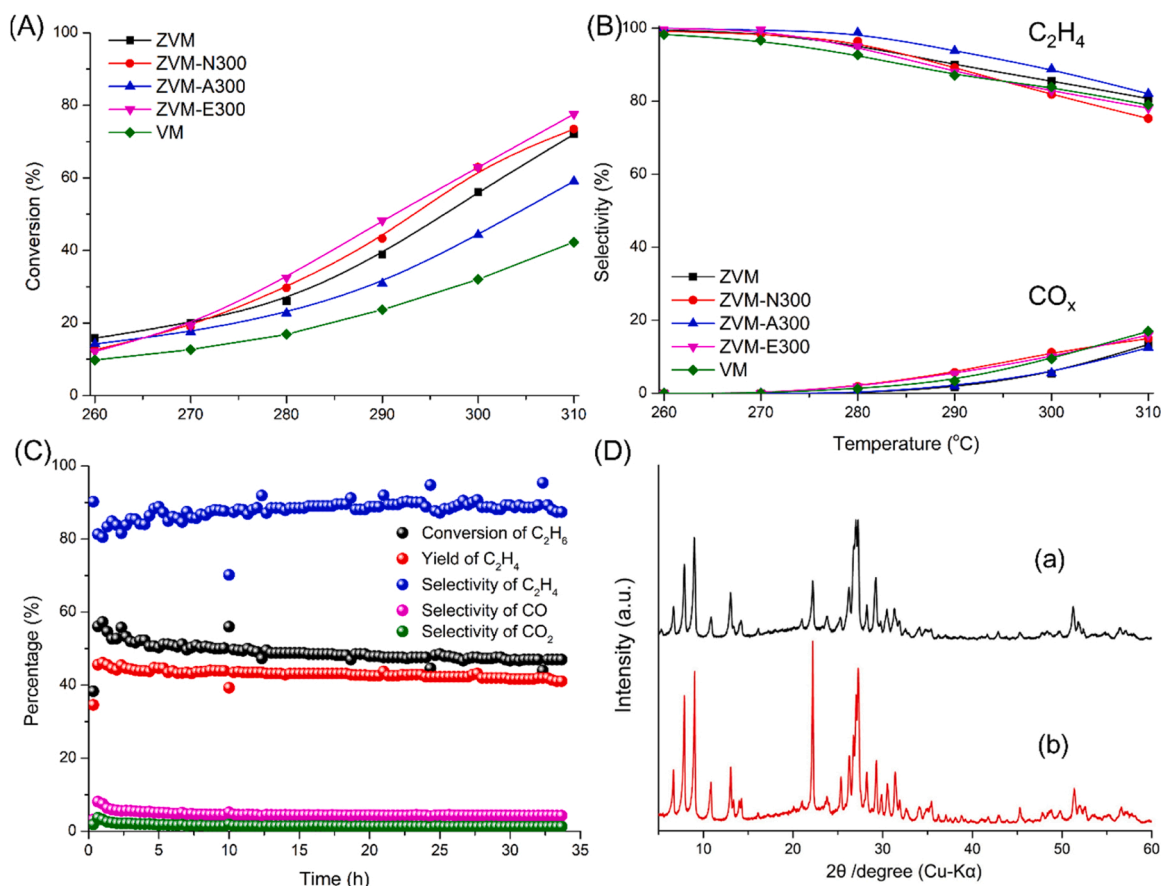
A **VM** supported Zn catalyst, **Zn-VM**, was synthesized using an impregnation method (see experimental for details) with almost the same Zn content to **ZVM**. XRD and FTIR of **Zn-VM** were unchanged compared to those of **VM** (Fig. S9A,B), indicating that impregnating Zn did not alter the structure of **VM**. There was no obvious particle being

observed in TEM image, and Zn signal was uniform in EDX-mapping, demonstrating that Zn was well-dispersed on **VM** (Fig. S10). The  $C_2H_6$  ODH activity of **Zn-VM** was lower than that of both **ZVM** and **VM**, suggesting that Zn on the external surface of **VM** did not activate **VM** (Fig. S9C,D). Further increasing the loading amount of Zn did not lead to increase the activity (Fig. S9).

V also affected the catalytic activity. **ZVM** with different V contents was synthesized. The reaction was carried out at 310 °C. The selectivity to  $C_2H_4$  decreased with increasing the V content of the catalysts while kept almost the same  $C_2H_6$  conversion (Fig. S11).

The pre-treatment condition affected the catalytic activity of **ZVM**. **ZVM** was treated in  $N_2$ , air, and  $C_2H_6$  for 2 h at 300 °C, forming **ZVM-N300**, **ZVM-A300**, and **ZVM-E300** (Fig. 1). Although the crystal structure of the catalyst was maintained after the treatments, the catalytic activity slightly changed. The catalytic activity of **ZVM-A300** decreased slightly, while the activity of **ZVM** treated with  $N_2$  and  $C_2H_6$  increased (Fig. 5A,B).

The stability of the catalyst was further tested for **ZVM**. The reaction was carried out for 35 h at 300 °C (Fig. 5C). The result showed that within the first 10 h the conversion of  $C_2H_6$  slightly decreased from 56 % to 50 %, while the selectivity to  $C_2H_4$  gradually increased from 84 % to 90 %. The yield of  $C_2H_4$  almost did not change in the first 10 h. After 10 h, the conversion of  $C_2H_6$  and selectivity to  $C_2H_4$  almost remained to be ca. 49 % and 92 %, indicating that the catalyst was stable. After the reaction, the catalyst was characterized by XRD, SEM, and XPS. XRD showed that the characteristic peaks of orthorhombic phase did not change after the catalytic reaction, indicating that the crystalline phase of the catalyst did not change (Fig. 5D). SEM showed that the morphology of the catalyst also did not change, remaining the rod-shape



**Fig. 5.**  $C_2H_6$  conversion (A) and product selectivity (B) of **ZVM**, **ZVM-N300**, **ZVM-A300**, **ZVM-E300**, and **VM** at different temperatures, (C) long-term stability of **ZVM**, (D) XRD patterns of (a) **ZVM** and (b) **ZVM** after the catalytic reaction, reaction conditions: 0.5 g of catalyst, 50 mL/min of total flow,  $C_2H_6/O_2/N_2 = 5/5/40$ , 260–310 °C of reaction temperature for (A) and (B), 300 °C of reaction temperature for (C), the carbon balance of all catalytic reactions being over 97 %.



(Fig. S12). XPS of the catalyst after the reaction (Fig. S13) revealed that the valences of Mo, V, and Zn almost did not change while OH content slightly increased. Additionally, the recyclability of the catalyst was also tested, which demonstrated that the catalyst could be reused (Fig. S14).

Compared with the reported  $C_2H_6$  ODH catalysts, ZVM displayed superior performance. ZVM exhibited the highest yield of  $C_2H_6$  at the lowest temperature among the reported catalysts (Fig. S15 and Table S3).

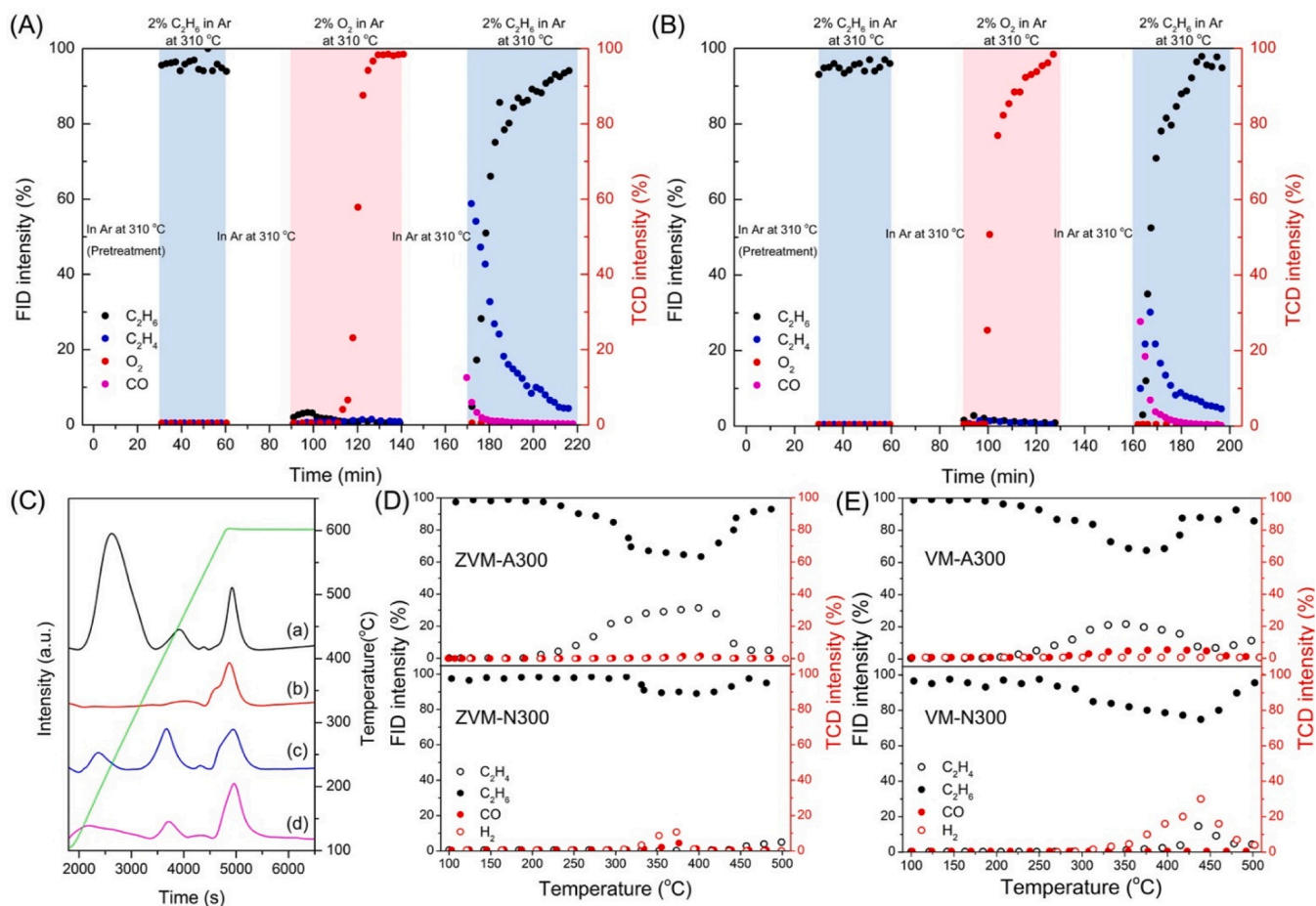
### 3.3. Reaction mechanism

The ODH of  $C_2H_6$  was conducted in a stepwise reaction to understand the reaction mechanism (Fig. 6A). Initially, ZVM was pretreated with Ar at 310 °C, followed by sequential purging of  $C_2H_6$ ,  $O_2$ , and  $C_2H_6$  at the same temperature. Ar purging was employed to remove any residual gases from the catalyst. The as-synthesized ZVM did not react with  $C_2H_6$  at 310 °C, as the  $C_2H_6$  signal was quickly detected upon introduction. When  $O_2$  was purged through the catalyst, the  $O_2$  signal was not observed for the first 20 min, indicating that  $O_2$  was consumed to oxidize ZVM. After  $O_2$  purging,  $C_2H_6$  was reintroduced, resulting in detection of both  $C_2H_4$  and CO signals, which gradually decreased as the reaction time was extended. In this stage, the oxidized ZVM reacted with  $C_2H_6$ , primarily forming  $C_2H_4$  and CO. The same experiment was conducted for VM (Fig. 6B). The phenomenon observed when VM was used as the catalyst was similar to that of ZVM, suggesting that the reaction mechanism might be the same. The difference was the reaction rate.  $O_2$  (8 min) and  $C_2H_6$  (3 min) were detected more rapidly than the case of ZVM, when they were introduced. Less  $C_2H_4$  but more CO were observed

compared to the case of ZVM. This indicated that Zn might not only activate  $C_2H_6$  but also  $O_2$ .

XPS analysis was conducted on ZVM with different treatments to know the changes in the oxidation state of Mo, V, and Zn in ZVM (Fig. 3). ZVM was treated in  $N_2$ , air, and  $C_2H_6$  at 300 °C. Mo was majorly  $Mo^{6+}$  in ZVM-N300 (Fig. 3Ab), and V was in the mixture of  $V^{5+}$  and  $V^{4+}$  with a ratio of 0.48 in ZVM-N300 (Fig. 3Bb). After calcination in air at 300 °C to form ZVM-A300, the peak of  $V^{5+}$  increased obviously with the ratio of  $V^{5+}/V^{4+} = 1.44$  (Fig. 3Bc). The oxidation state of Mo and Zn did not change after calcination at 300 °C. Following the air treatment,  $C_2H_6$  was used to treat ZVM-A300, and the results indicated that  $V^{5+}$  was reduced to  $V^{4+}$  without any changes in Mo and Zn. Therefore, only V underwent a change in oxidation state during the reaction. Thus, the redox of V from  $V^{4+}$  to  $V^{5+}$  was crucial in achieving high activity for  $C_2H_6$  ODH. To further confirm the importance of  $V^{5+}$  for  $C_2H_6$  ODH, ZVM-A300 (0.5 g) was treated with an aqueous solution of  $N_2H_4SO_4$  (0.25 mol/L, 15 mL) at room temperature to reduce  $V^{5+}$ , and the resulting catalyst was denoted as ZVM-A300- $N_2H_6$ . XRD and FTIR showed that the basic structure of ZVM-A300 did not change (Fig. S16). XPS showed that V valence changed from  $V^{5+}$  to  $V^{4+}$  without change of O (Fig. S17). This indicated that oxygen species of ZVM-A300 and ZVM-A300- $N_2H_6$  were the same. The only difference was V valence. ZVM-A300- $N_2H_6$  did not react with  $C_2H_6$  (Fig. S18), demonstrating that  $V^{5+}$  was critical for  $C_2H_6$  ODH. The previous studies showed that V species are the active sites for the first C-H bond activation in  $C_2H_6$  activation [60–62], while Mo does not significantly impact on  $C_2H_6$  activation [63], which is in good agreement with our results.

Furthermore, the XPS peak of  $O_{1s}$  could be fitted with the peaks at



**Fig. 6.** The stepwise reaction of  $C_2H_6$  ODH catalyzed by (A) ZVM and (B) VM, reaction condition: catalyst 0.5 g, Ar 30 mL/min, (C) TPO profiles of (a) ZVM-N300, (b) ZVM-A300, (c) VM-N300, and (d) VM-A300, (D) TP- $C_2H_6$  profiles of ZVM-A300 and ZVM-N300, and (E) TP- $C_2H_6$  profiles of VM-A300 and VM-N300.



530.35 eV, 531.6 eV, and 533.5 eV, corresponding to lattice oxygen ( $O_{lat}$ ), lattice OH (OH), and adsorption oxygen ( $O_{ads}$ ) in the material (Fig. 3C) [58]. There was majorly lattice  $O_{lat}$  with only few OH being observed in ZVM-N300 (Fig. 3Cb). After the oxidation of ZVM at 300 °C in air, the peak areas and positions of  $O_{lat}$  and OH remained unchanged, indicating saturation of lattice oxygen in the fresh catalyst (Fig. 3Cc). When the catalyst was treated with  $C_2H_6$ , the peak of OH appeared, indicating the formation of OH (Fig. 3Cd) [64]. ZVM-A300 was treated with  $C_2H_6$  and the resulting catalyst (ZVM-AE300) showed the obvious OH and  $O_{ads}$  signals (Fig. 3Ce), demonstrating that  $C_2H_6$  dehydrogenation occurred on ZVM-A300. OH formed by transferring H from  $C_2H_6$  to  $O_{lat}$  with forming some oxidized organic species as  $O_{ads}$ . The FTIR peak at 3560  $cm^{-1}$  of ZVM and VM was attributed to O-H, which was in good agreement with XPS (Fig. S19). TPD of ZVM-E300 revealed that there were three main peaks with the positions at 220, 460, and 520 °C (Fig. S20). The presence of the desorption indicated the dehydration of OH at the temperatures forming the oxygen vacancies ( $O_v$ ). At the current reaction temperature (260–310 °C), only partial OH was able to be transferred to  $O_v$ . The results demonstrated that when  $C_2H_6$  reacted with the catalyst,  $O_{lat}$  of the catalyst transferred to OH, which then dehydrated to form  $O_v$ . The existence of  $O_v$  after the catalyst was treated with  $C_2H_6$  was further confirmed by EPR, showing the peak at 3510 G with g of 2.0046 attributed to  $O_v$  (Fig. S21A).

Furthermore, in situ FTIR measurements were carried out for ZVM-A300 and VM-A300 at 300 °C (Fig. 7A,B). After introducing  $C_2H_6$ , the bands at 2800–3100  $cm^{-1}$  and 1250–1650  $cm^{-1}$  corresponded to C-H stretching mode and bending mode of  $C_2H_6$ , respectively. The bands at 3251, 3325, and 3560  $cm^{-1}$  were attributed to OH attached to the metal ions (M-OH), which were derived from dehydrogenating  $C_2H_6$  with the catalysts (Fig. 7A) [65–67]. Notably, in comparison to VM, the peak at

3325  $cm^{-1}$  was exclusive in ZVM, possibly indicating OH binding to Zn. Upon saturation with  $C_2H_6$ ,  $N_2$  was introduced for  $C_2H_6$  desorption, revealing that the bands for  $C_2H_6$  obviously decreased, indicating that the free  $C_2H_6$  was removed by  $N_2$  purging. However, the remaining peaks for OH indicated that OH could not be removed completely by  $N_2$ . The persistence of C-H bond peaks suggested the formation of intermediates strongly bound to the catalysts. The position of peak at 1540  $cm^{-1}$  for the C-H bond in ZVM was different from that in VM, indicating that intermediates interacted with Zn in a distinct binding state compared to the case of VM. After  $O_2$  purging, all the remaining peaks disappeared, indicating that OH was disappeared which might be transfer to  $O_{lat}$  and the intermediates were removed from the catalysts by  $O_2$ . The in situ FTIR demonstrated the formation of intermediates during the reaction and  $O_{lat}$  would be recovered by  $O_2$ .

To test whether any reactive oxygen species, such as  $\cdot O_2$  and  $\cdot OH$ , were generated during air calcination, the quenching experiment was conducted.  $CHCl_3$  and isopropanol (IPA) were used to quench  $\cdot O_2$  and  $\cdot OH$  [68,69], respectively. ZVM-A300 (0.5 g) was treated with  $CHCl_3$  (10 mL) followed by treatment with a 10 % IPA aqueous solution (1.66 mol/L, 200 mL). The resulting catalyst was denoted as ZVM-A300-quencher. XRD and FTIR of ZVM-A300-quencher were almost the same to those of ZVM-A300, indicating that the structure of the catalyst remained unchanged after the quenching experiment (Fig. S22).  $C_2H_6$  oxidation by ZVM-A300-quencher showed that  $C_2H_6$  was consumed at the beginning and the performance of ZVM-A300-quencher was similar to that of ZVM-A300, demonstrating that the quenching experiment did not affect the activity of the catalyst (Fig. S23). Moreover, ZVM-A300 was characterized by EPR (Fig. S21B), showing that reactive oxygen species was essentially absent from the catalyst. Therefore, there was no reactive active species generated [70,

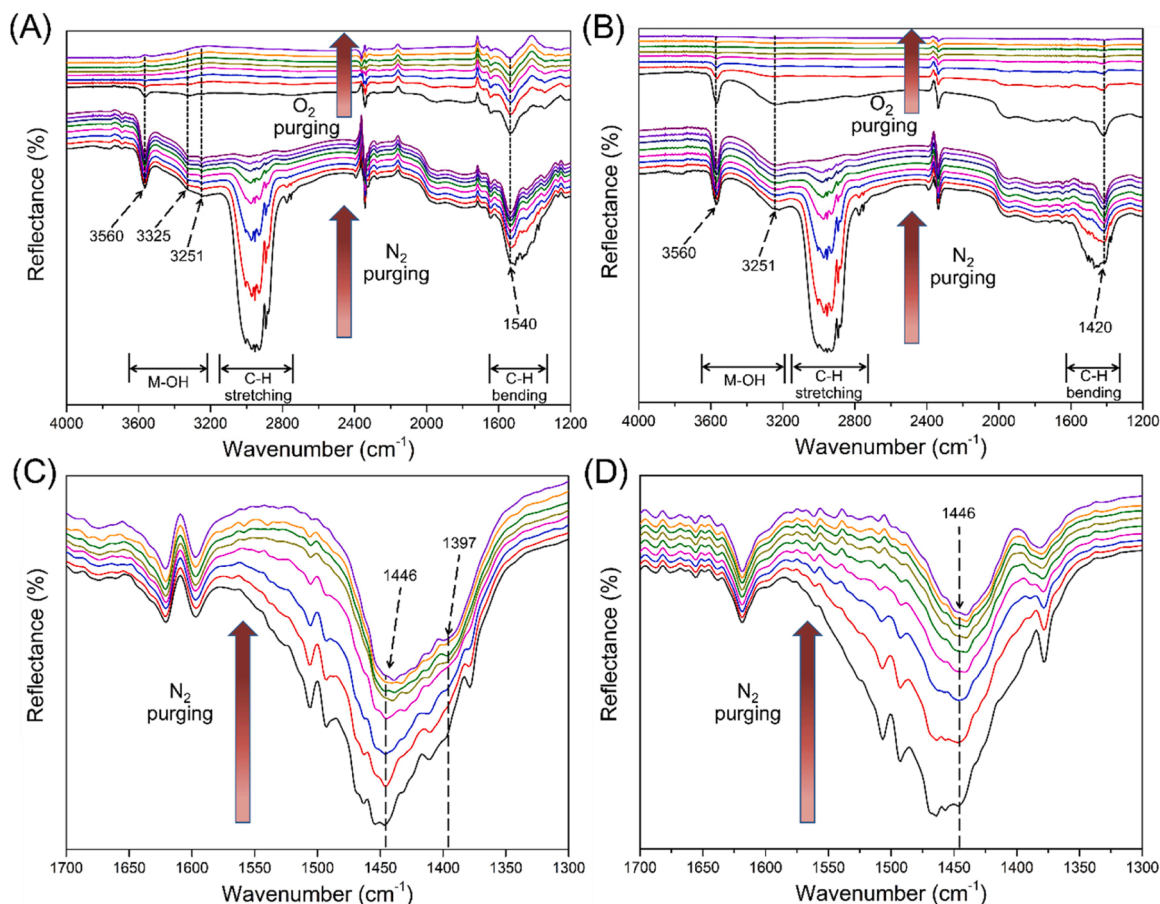


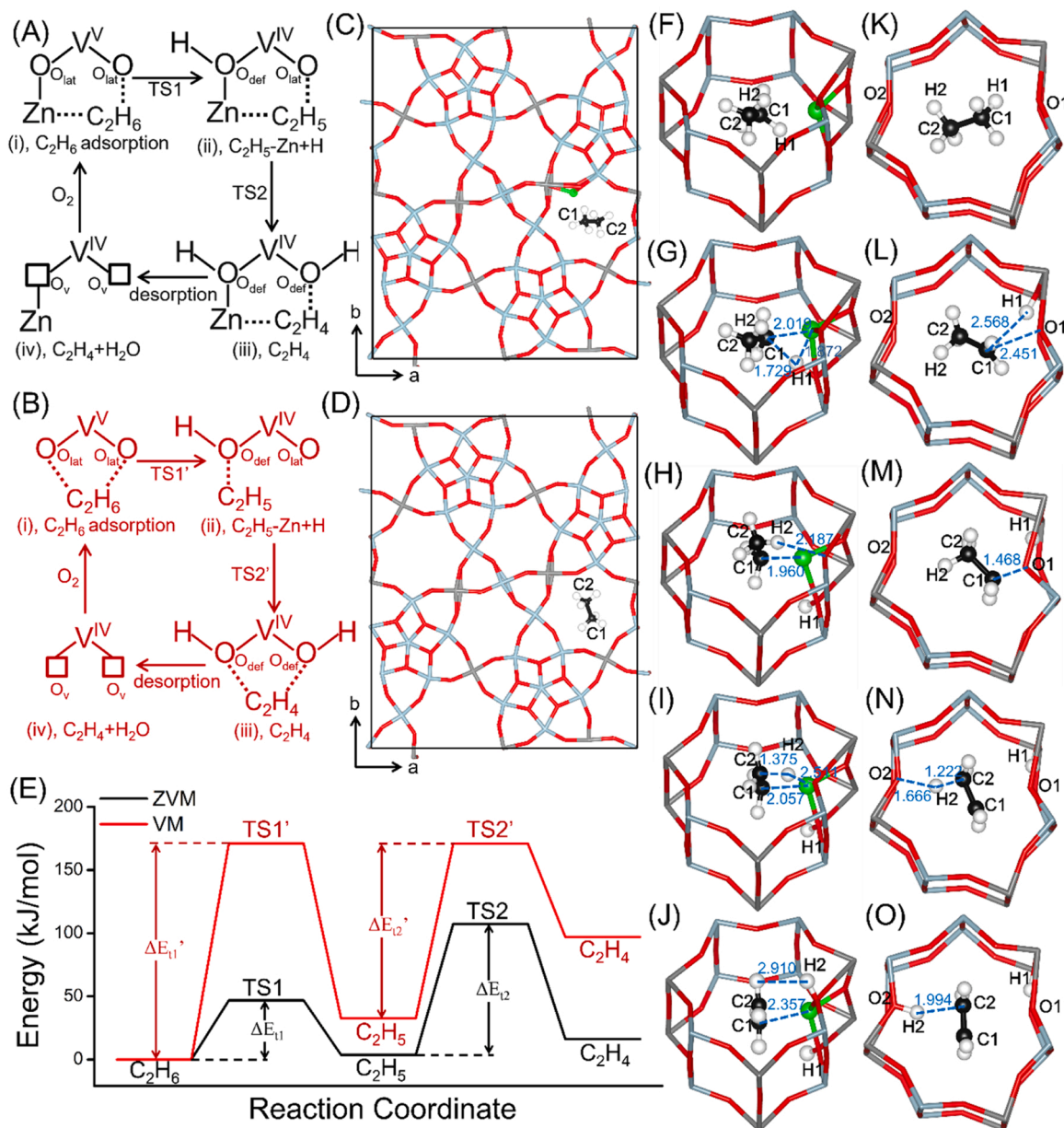
Fig. 7. In situ FTIR of  $C_2H_6$  in (A) ZVM and (B) VM at 300 °C under  $N_2$  flow or  $O_2$  flow, in situ FTIR of  $C_2H_6$  on (C) ZVM and (D) VM at 25 °C under  $N_2$  flow.

71].

Based on the results presented above, a reaction pathway was proposed. The reaction mechanism of **ZVM** for  $C_2H_6$  ODH was similar to Mars-Van Krevelen (MvK) Mechanism [33,72–75]. The as-synthesized **ZVM** was oxidized by  $O_2$  to form the oxidized **ZVM** with increasing the valence of  $V^{4+}$  to  $V^{5+}$ . The oxidized **ZVM** extracted H from  $C_2H_6$  to form intermediates that bound to the catalyst, forming OH that were bound to the framework of **ZVM**. The intermediates then decomposed to produce  $C_2H_4$ , and V in **ZVM** was subsequently reduced to  $V^{4+}$  again (Fig. 8A). OH might dehydrate with H to form  $O_v$  on the catalyst, which was able to be recovered by  $O_2$  oxidation. The proposed reaction mechanism of **ZVM** was similar to that of the most of reported Mo and V based  $C_2H_6$  ODH catalysts (Table S4).

To confirm the role of Zn, TPO and TP- $C_2H_6$  were conducted for **ZVM**. The redox property of the material was investigated by TPO (Fig. 6C). In the TPO profiles of **ZVM-N300** and **VM-N300**, three main

peaks were observed at 270, 400, and 600 °C, corresponding to three different reductive species in the catalysts. The reduction species at 270 °C were related to  $C_2H_6$  ODH, given its proximity to the reaction temperature. Compared with **VM**, the peak of **ZVM-N300** at 270 °C was larger, which indicated that the incorporation of Zn activated  $O_2$  and facilitated the oxidation of more reductive species at a low temperature (270 °C). Furthermore, TPO investigations were conducted using **ZVM-A300** and **VM-A300**. The result showed that the peak at 270 °C disappeared, indicating that the species was oxidized under calcination at 300 °C while the peak at 400 and 600 °C remained unchanged. From XPS,  $V^{4+}$  was oxidized to  $V^{5+}$  at 300 °C (Fig. 3B), and thus the TPO peak at 270 °C was attributed to the oxidation of  $V^{4+}$ . TPO of **ZVM-E300** and **VM-E300**, the peak at 200–300 °C of **ZVM-E300** was at a lower temperature, indicating that Zn incorporation might activate  $O_2$ , which caused easier oxidation of the reduced catalysts (Fig. S24). DSC confirmed that the reactions between  $O_2$  and the catalysts were



**Fig. 8.** Proposed reaction pathway of  $C_2H_6$  ODH catalyzed by (A) **ZVM** and (B) **VM**, (C)  $C_2H_6$  in unit cell of **ZVM**, (D)  $C_2H_6$  in unit cell of **VM**, (E) energies of the intermediates and the transition states of  $C_2H_6$  dehydrogenation based on DFT calculations, structure models of the intermediates and the transition states of  $C_2H_6$  dehydrogenation, (F)  $C_2H_6$  in **ZVM**, (G) TS1 in **ZVM**, (H)  $C_2H_5$  in **ZVM**, (I) TS2 in **ZVM**, (J)  $C_2H_4$  in **ZVM**, (K)  $C_2H_6$  in **VM**, (L) TS1' in **VM**; (M)  $C_2H_5$  in **VM**, (N) TS2' in **VM**, (O)  $C_2H_4$  in **VM**, Mo (blue), V (gray), O (red), Zn (green), C (black), H (white).

exothermic, with **ZVM** exhibiting a higher heat release compared to **VM**, indicating that **ZVM** preferentially reacted with  $O_2$  (Fig. S25). Therefore, Zn caused oxidizing  $V^{4+}$  in the material at a low temperature much easier (270 °C).

The interaction of  $O_2$  and the catalysts was simulated by the DFT calculation. The charge density difference (CDD) of  $O_2$  adsorbed in the heptagonal channel of the catalysts were calculated (Fig. 9). An increase in charge density was observed between Zn and O while a decrease in charge density was observed between O-O of  $O_2$ , indicating that the O-O bond was weakened in **ZVM** (Fig. 9A,B). In the case of **VM**, although  $O_2$  also located in the heptagonal channel, the charge density was much smaller than in the case of **ZVM**, indicating that  $O_2$  was weakly affected by **VM** (Fig. 9C,D). Therefore, Zn caused activation of  $O_2$ , leading to oxidation of  $V^{4+}$  in the material at a low temperature.

TP-C $_2$ H $_6$  were conducted (Fig. 6D, E). For **ZVM-N300**, there were no C $_2$ H $_6$  signal decreases in the TP-C $_2$ H $_6$  profiles at 200 °C, demonstrating that C $_2$ H $_6$  did not reacted with the catalyst at low temperatures. Further increasing the temperature to over 320 °C caused the catalyst to react with C $_2$ H $_6$ , possibly due to the reaction between  $O_{lat}$  of the catalyst and C $_2$ H $_6$ . **ZVM-N300** was not active for reacting with C $_2$ H $_6$  at low temperatures. Air treatment activated the catalyst. **ZVM-A300** showed a decrease in the C $_2$ H $_6$  signal at 200 °C, along with the appearance of products peaks of C $_2$ H $_4$  and CO, indicating that the catalyst reacted with C $_2$ H $_6$  at low temperatures. Similar to **ZVM-N300**, **VM-N300** did not show the peak at low temperatures, and only **VM-A300** showed the signal. The peak of **VM-A300** was smaller than that of **ZVM-A300**, indicating that Zn also activated C $_2$ H $_6$ .

The charge density difference (CDD) of C $_2$ H $_6$  in the micropores of the catalysts was calculated, showing the charge enrichment and depletion of C $_2$ H $_6$  after adsorption (Fig. 9). The charge density between C of C $_2$ H $_6$  and Zn of the catalyst increased, while it decreased between the C-H bond of C $_2$ H $_6$  (Fig. 9E, F). This indicated that the C-H bond of C $_2$ H $_6$  was weakened due to interaction with Zn. For **VM**, the charge densities of both charge increasing and decreasing were smaller, indicating weak interaction between C $_2$ H $_6$  and **VM** (Fig. 9G, H). Moreover, the in situ FTIR spectra of C $_2$ H $_6$  in **ZVM** and **VM** at 25 °C showed that the peak shifted to a lower wavenumber (1397 cm $^{-1}$ ) in **ZVM** (Fig. 7C,D), indicating that the C-H bond of C $_2$ H $_6$  in **ZVM** was longer than that in **VM**. This also indicated that the C-H bond was weakened by **ZVM**. CDD also showed that the charge density of O nearby Zn increased, indicating that H affinity of O increased after Zn incorporation, which enhanced the activity of dehydrogenation (Fig. S26).

To further understand the role of Zn during the reaction, we investigated the structures of the intermediates and transition states at each

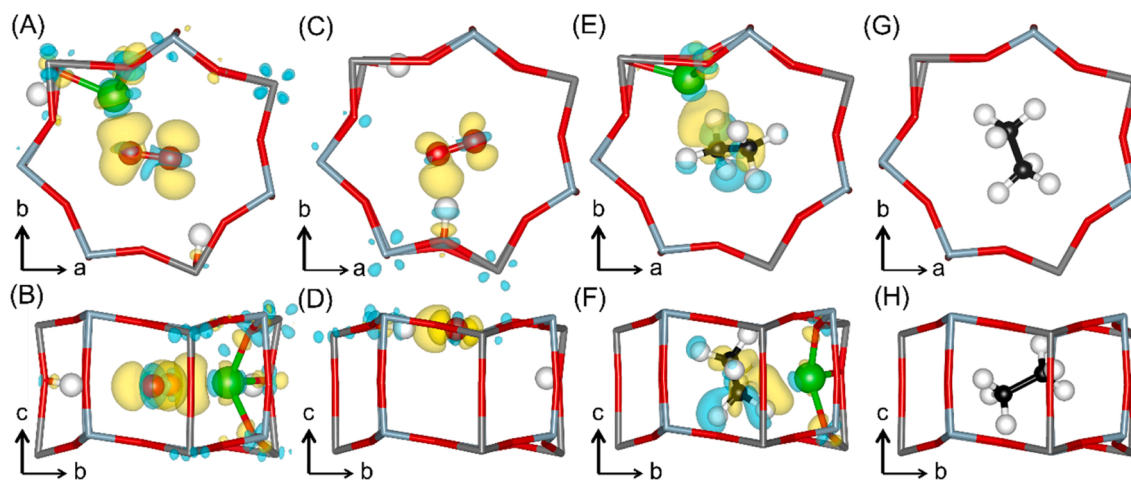
step of C $_2$ H $_6$  ODH over **ZVM** and **VM** (Fig. 8). The structure of **ZVM** and **VM** were optimized. The catalytic reaction occurred within the heptagonal channel of the catalysts [53]. The energies and structures of intermediates and transition states of C $_2$ H $_6$  inside the heptagonal channel were obtained. The static binding energy was calculated using PBE and PBE-D3 correction. With D3 correction, the system energy decreased further, indicating the presence of van der Waals interactions between the catalyst and C $_2$ H $_6$  (Fig. S27).

According to the above discussion, H of C $_2$ H $_6$  was extracted by the catalyst and migrated to the framework of the catalyst. The exact position of H was estimated by the DFT calculation. The result showed that H at V-OH revealed obviously lower energy (Fig. S28), indicating that these sites were suitable for H extraction.

For **ZVM**, adsorbed C $_2$ H $_6$  was located nearby Zn in the heptagonal channel of the catalyst (Fig. 8C). According to the CDD images, the C-H bond was weakened in the catalyst by interacting with Zn (Fig. 9E, F). Dehydrogenation of C $_2$ H $_6$  occurred with substrate H1 from C $_2$ H $_6$  to the O atom of the framework, forming the intermediate of C $_2$ H $_5$  coordinating to Zn with a distance of C1-Zn of 1.960 Å (Fig. 8H). The energy of the intermediate increased to 3.7 kJ/mol (Fig. 8E). The transition state (TS1) was optimized. H1 interacted with C $_2$ H $_5$  and Zn with distances of C1-H1 and H1-Zn of 1.729 and 1.872 Å, and C1 interacted with Zn at a distance of 2.019 Å (Fig. 8G). Zn assisted in transferring H from C $_2$ H $_6$  to the framework of **ZVM**. The energy of the transition state and the activation energy ( $\Delta E_{t1}$ ) was 46.8 kJ/mol. H2 of C $_2$ H $_5$  then transferred to the framework, forming the product of C $_2$ H $_4$  coordinating with Zn at a distance of 2.357 Å (Fig. 8J). The system energy of the product was 16.2 kJ/mol. The transition state (TS2) revealed that Zn interacted with C $_2$ H $_5$ . H2 of C $_2$ H $_5$  interacted with C2 and Zn at distances of 1.375 Å and 2.511 Å (Fig. 8I). The energy of TS2 was 107.4 kJ/mol, with  $\Delta E_{t2}$  of 103.7 kJ/mol (Fig. 8E).

In the case of **VM**, the reaction also occurred in the heptagonal channel. The intermediate of C $_2$ H $_5$  also formed. Different from the case of **ZVM**, C1 of the intermediate interacted with O1 of **VM** at a distance of C1-O1 of 1.468 Å, with a system energy of 32.7 kJ/mol (Fig. 8E). The transition state (TS1') showed that H1 transferred with a distance of H1-C1 of 2.568 Å (Fig. 8E,K,L). The energy of TS1' for **VM** was 171.2 kJ/mol, with  $\Delta E_{t1}'$  of 171.2 kJ/mol, which was higher than the energy of  $\Delta E_{t1}$  for **ZVM** (46.8 kJ/mol) (Fig. 8E). Then, H2 migrated to O2 of the framework, forming the product of C $_2$ H $_4$  with an energy of 97.1 kJ/mol (Fig. 8E,M,N,O). TS2' of **VM** was optimized, showing an energy of 170.9 kJ/mol with  $\Delta E_{t2}'$  of 138.3 kJ/mol, also higher than the case of **ZVM** ( $\Delta E_{t2}$ =103.7 kJ/mol) (Fig. 8E).

Thus, Zn incorporation decreased the system energy of the



**Fig. 9.** The CDD images of  $O_2$  adsorbed in the heptagonal channel of (A) and (B) **ZVM**, (C) and (D) **VM**, the CDD images of  $C_2H_6$  adsorbed in the heptagonal channel of (E) and (F) **ZVM**, (G) and (H) **VM**. The yellow and blue isosurfaces indicating the charge gain and depletion, (isosurfaces=0.002), Mo (blue), V (gray), O (red), Zn (green), C (black), H (white).



intermediates as well as the transition state by the close interaction of Zn with  $C_2H_5$ , which was the reason that the activity of ZVM was higher than that of VM.

To further confirm the  $C_2H_6$  ODH over the catalysts based on simulation, the reaction kinetic was investigated. First of all, factors related to transport limitations were explored by varying the total flow rate and granularity. The reaction performance remained unchanged, indicating that the transport limitations did not affect the reaction (Fig. S29). Both catalysts exhibited a similar dependence of partial pressure of  $C_2H_6$  (0.5 for VM and 0.7 for ZVM) regarding the reaction rate (Fig. S2), while VM displayed a higher dependency on the partial pressure of  $O_2$  (0.4) compared to ZVM (0.2). The experimental activation energy was calculated based on Arrhenius equation. The result showed that the experimental activation energy of ZVM was 92 kJ/mol, which was lower than that of VM (142 kJ/mol). This trend was consistent with the DFT calculation, indicating the reasonableness of simulation.

Recovery of the catalyst and the formation of water were simulated (Fig. S30). There were majorly two routes for water formation. In route 1, water was formed by dehydration of a lattice oxygen with two H from  $C_2H_6$ , and  $O_2$  compensated for the lattice oxygen vacancy ( $O_v$ ). The other route indicated that the adsorbed  $O_2$  reacted with H, forming water directly. EPR analysis of ZVM-E300 confirmed the existence of  $O_v$ , demonstrating that route 1 might be the preferred pathway for dehydration (Fig. S21A).

Total oxidation of  $C_2H_6$  ODH was investigated by the oxidation of  $C_2H_4$ . For ZVM,  $C_2H_4$  conversion obviously increased when the temperature was over 340 °C, indicating that total oxidation majorly occurred above 340 °C. ZVM exhibited a higher temperature for total oxidation compared to VM (280 °C), suggesting that Zn might suppress total oxidation and increase  $C_2H_4$  selectivity at lower temperatures (Fig. S31). The mechanism of total oxidation was simulated using DFT calculation. Both MvK and Langmuir-Hinshelwood (LH) mechanisms were tested (Fig. S32). MvK mechanism indicated that the energy of dehydrogenation product ( $C_2H_4$ ) was lower than the energy of the total oxidation intermediate ( $CH_3CHO$ ) [76,77]. In contrast, LH mechanism showed a different result from MvK mechanism, with the energy of the total oxidation intermediate being lower. At lower temperatures,  $C_2H_4$  was the major product, but as the temperature increased,  $CO_2$  selectivity increased. Therefore,  $C_2H_6$  ODH majorly followed MvK mechanism at lower temperatures, while total oxidation followed LH mechanism at higher temperatures.

#### 4. Conclusion

In summary, the Zn incorporated vanadomolybdate was synthesized for  $C_2H_6$  ODH. The incorporation of Zn did not change the structure of the material. Zn was found to be located in the heptagonal channel of the material, as determined by the powder XRD and the DFT calculation. Zn incorporation activated both  $O_2$  and  $C_2H_6$ , causing oxidation of V in the material and  $C_2H_6$  ODH at a lower temperature. The catalytic activity of ZVM for  $C_2H_6$  ODH (45 % of  $C_2H_4$  yield) was higher than that of VM without Zn (26 % of  $C_2H_4$  yield) at the same temperature, highlighting the essential role of Zn in achieving high catalytic activity. The reaction mechanism study revealed that Zn played a key role in coordinating the intermediate of  $C_2H_5$  and stabilizing it, as well as stabilizing the transition state of the reaction catalyst by the material.

#### CRediT authorship contribution statement

Conceptualization: Zhenxin Zhang. Funding acquisition: Zhenxin Zhang, Qianqian Zhu, Yanshuo Li. Investigation: Bolun Yu, Denan Li, Shufan Yao, Lifeng Zhang. Supervision: Zhenxin Zhang, Qianqian Zhu, Yanshuo Li. Writing – original draft: Bolun Yu, Zhenxin Zhang. Writing – review & editing: Qianqian Zhu, Zhenxin Zhang.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123463.

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